

# **Effect of Compositional Short Range Order on Glass Formation in Binary Metallic System**

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## **ABSTRACT**

Molecular Dynamics simulation was carried out to study the glass transition and crystallization in the metal-metalloid binary system with pair-wise potentials. The results show that a repulsive potential between metalloid (small) atoms increases the glass forming ability. The observation is consistent with the recent theory of bulk metallic glass formation through local glass transition and nano-glass formation. The theory predicted that the compositional short-range order (CSRO) prevents the small atom pairing so as to increase the glass forming ability (GFA). The present results demonstrate the important role of CSRO in bulk metallic glass formation.

## **INTRODUCTION**

The recent development of bulk metallic glass has drawn tremendous interest in both technological applications and fundamental research of metallic glasses. Since Duwez [1] fabricated the first amorphous metallic alloy Au<sub>75</sub>Si<sub>25</sub> by using the rapid solidification technique in 1959, the glass forming ability has been greatly improved, seen from the critical cooling rate increasing from 10<sup>6</sup> K/s to 1 K/s. It has been found that various factors, such as the atomic size ratio, composition, and interatomic potential, affect the GFA of metallic systems, while the underlying microscopic mechanism of how to improve GFA remains a major challenge in theoretical research. Recently, Egami [2] proposed a theory of bulk metallic glass formation based on the idea of local glass transition. This theory suggests that GFA is improved if the glass transition does not take place at a single temperature for bulk metallic glasses and there are series of local glass transitions, which are distributed over a wide temperature range. The GFA depends on the width of the temperature range, which can be enlarged by introducing large size difference ratio and CSRO. In this paper, we describe the results of molecular dynamics simulation which prove that the presence of CSRO improves the GFA of metallic systems.

## **COMPUTATION PROCEDURE**

We performed constant number, pressure and temperature (NPT) molecular dynamics simulation on a binary AB system composed of 500 particles, 400 "A" and 100 "B" atoms representing a metal-metalloid binary system. We cooled the system from 1800 K to 600K at a cooling rate of  $2 \times 10^{13}$  K/s. The time step is  $1 \times 10^{-3}$  ps, and  $5 \times 10^4$  steps are used for equilibrating the system and additional  $5 \times 10^4$  steps for collecting the data of interest. Since the purpose of this study is to examine the general principles of the atomic size effect and not to simulate any particular alloy, simple model potentials were used to describe the system. The transition metal atom "A" has the atomic size and mass of iron atom, and the modified Johnson's potential is used

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1. REPORT DATE <b>2002</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>			
<b>4. TITLE AND SUBTITLE</b> <b>Effect of Compositional Short Range Order on Glass Formation in Binary Metallic System</b>			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
<b>6. AUTHOR(S)</b>			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> <b>Department of Materials Science and Engineering, University of Pennsylvania Philadelphia, Pa 19104-6272, U.S.A.</b>			8. PERFORMING ORGANIZATION REPORT NUMBER		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> <b>Approved for public release, distribution unlimited</b>					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b>					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b> a. REPORT <b>unclassified</b>			<b>17. LIMITATION OF ABSTRACT</b> <b>UU</b>	<b>18. NUMBER OF PAGES</b> <b>6</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
b. ABSTRACT <b>unclassified</b>					
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to describe its interaction. The metalloid atom “B” has the same mass as “A”, but a smaller size. The size scaled modified Johnson’s potential is used to describe the *A-B* interaction. The *B-B* interaction is described by two different schemes, the modified Johnson’s potential [3,4] or a decreasing exponential potential, which introduces the CSRO.

## RESULTS

Figure 1 shows the potentials we used for describing the binary system without CSRO: The modified Johnson’s potential for *A-A*, and the size scaled modified Johnson’s potential for both *A-B* and *B-B*, keeping the depth constant. Under this potential scheme, we changed the size difference ratio of “A” and “B” atoms in the metallic system to study the transition in the quenching process. Figure 2 is the volume change of the system with temperature. For the system with the size difference ratio of 10% and 12%, the volume has a jump at temperatures of 1250 K and 1125 K, respectively. The discontinuous volume change is a sign of crystallization. The crystallization temperature becomes lower when the size difference ratio is increased. For the two systems with larger size difference ratio of 14% and 15%, the volume change is continuous. The glass transition is not a real phase transition, so volume change is continuous in quenching. The kink in the volume curve indicates the glass transition. The system with a 15% size difference ratio has an apparent glass transition at 1050 K, and that with a 14% at 900 K. Figure 3 is the RDF for the systems with 14% and 12% size difference ratios at 1800K, showing the system is completely melted. Figure 4 shows that the RDFs of the two systems at 600K are obviously different at the second peak. For the system with a 14% size difference ratio, the second peak is well separated into two sub-peaks, which are corresponding to the second and third nearest neighbors of the BCC Fe structure. For the system with a 12% size difference ratio, the second peak has a small split, which indicates the characteristics of glass. The simulation of 13% size difference ratio system shows that glass transition and crystallization happen without reproducibility. Thus the critical size difference for glass formation determined by this simulation is 13%.

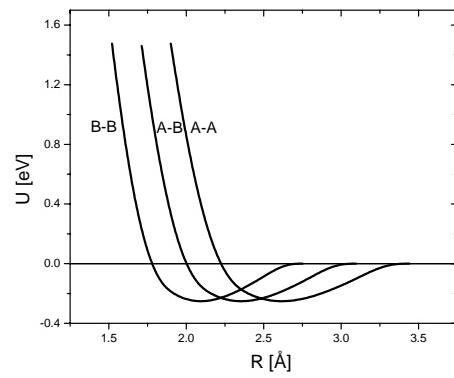


Figure 1. Modified Johnson's potential on *A-A*, and Sized scaled Johnson's potential for *A-B* and *B-B* (No compositional short range order).

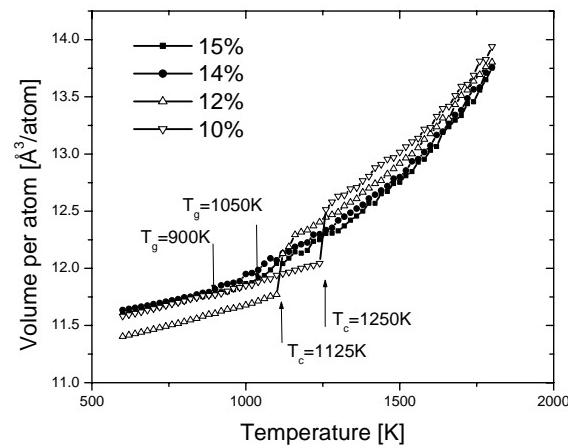


Figure 2. Volume change with temperature for metallic systems with different size ratio.

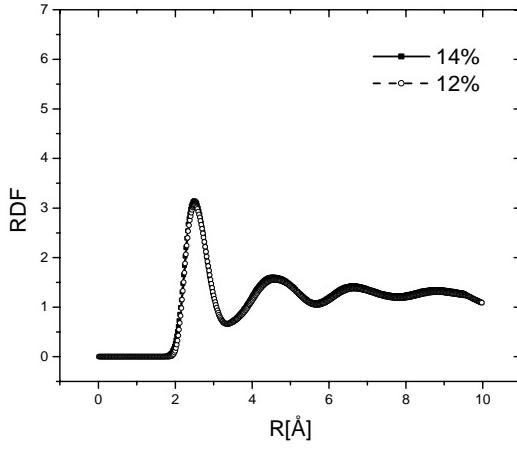


Figure 3. RDF indicating liquid structure for the system with 14% and 12% size difference ratios

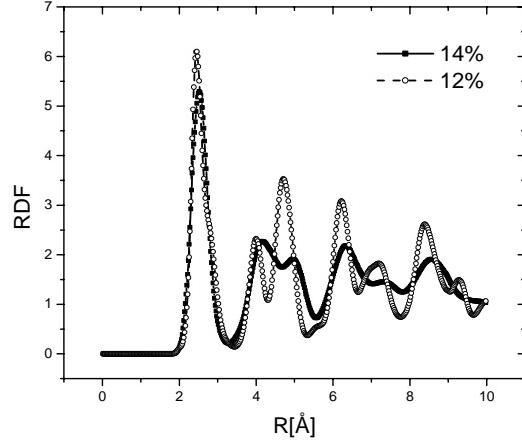


Figure 4. RDF indicating a crystal structure for 12% size difference ratio and a glass structure for 14% size difference ratio. (No compositional short range order)

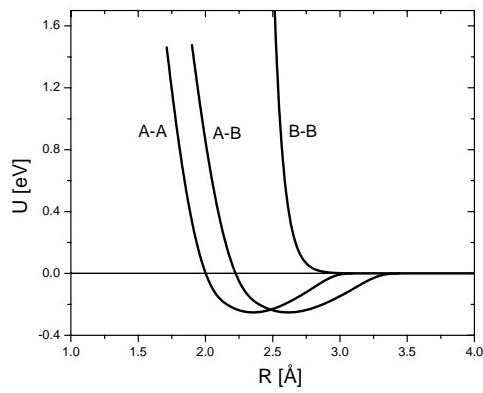


Figure 5. Modified Johnson's potential for A-A, and sized scaled Johnson's potential for A-B and repulsive exponential for B-B. (Compositional short range order exists)

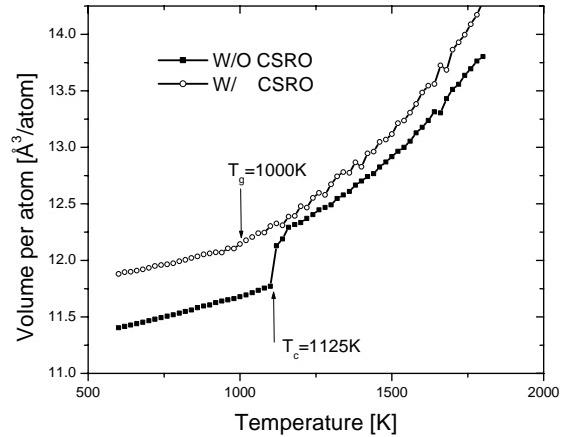


Figure 6. Volume change with temperature for the system with a 12% size difference ratio (glass transition with CSRO, crystallization without CSRO).

In order to study the effects of the CSRO, we introduced a repulsive exponential potential on *B-B* pair. This potential produces a very strong repulsive force between the *B-B* first nearest neighbors, so it can prevent a contact of *B* and *B* atoms. Figure 5 is the potentials we used in describing the atomic interaction. The interactions for A-A and A-B are the same as before, and only the B-B interaction is changed. As shown above the binary system without CSRO crystallizes at the cooling rate of  $2 \times 10^{13}$  K/s when the size difference is 12%. However, after the CSRO is introduced a glass transition occurs. Figure 6 is the volume change with the temperature of the me-

talic system before and after introducing the chemical short-range order. The volume has a continuous change with temperature with the presence of the CSRO, which indicates a glass transition, with the glass transition temperature of 1000 K. Figure 7 shows the RDF at 600 K for the two metallic systems. The clear difference in the split of the second peak indicates that different transitions take place in the quenching process.

## DISCUSSION

The critical size difference for glass formation for the system without CSRO, 13 %, correspond to the volume ratio of  $\Delta V/\langle V \rangle = 0.367$ , where  $\Delta V = V_A - V_B$ ,  $\langle V \rangle = C_A V_A + C_B V_B$ ,  $V_A$  and  $V_B$  are the atomic volume for A and B, and  $C_A$  and  $C_B$  are the atomic compositions of A and B. This gives the size ratio factor,

$$C_B^{\min} \frac{\Delta V}{\langle V \rangle} = 0.073 , \quad (1)$$

where  $C_B^{\min}$  is the minimum concentration of B element for glass formation, rather than 0.1 for the experimental and theoretical size factor [5]. This must be due to the rapid cooling rate of the simulation. Generally, the higher the cooling rate the more stable glasses are. As stated by D. Turnbull, any material becomes a glass if it is cooled from the liquid state fast enough [6]. Thus this much of underestimate of the critical alloy composition/size difference is not surprising. This, however, is the most critical shortcoming of the MD simulation in evaluating the GFA. The MD simulation can provide insights and trends, but not quantitative information as far as GFA is concerned.

The effect of the CSRO introduced by applying the repulsive exponential potential on small B-B atoms is to prevent the B-B pairs. Figure 8 is the partial RDF of “B” atoms at 600 K with the repulsive potential and the size scaled modified Johnson’s potential. Under the repulsive potential, there is no first nearest neighbor of B-B atoms, which means “B” atom is surrounded only by “A” atoms. The volume and RDF evolution with temperature show that the existence of the CSRO helps glass transition over the crystallization.

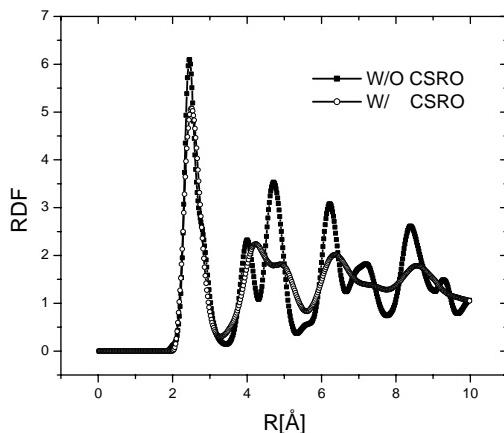


Figure 7. RDF at 600K for the system with a 12% size difference ratio (glass transition with CSRO, crystallization without CSRO)

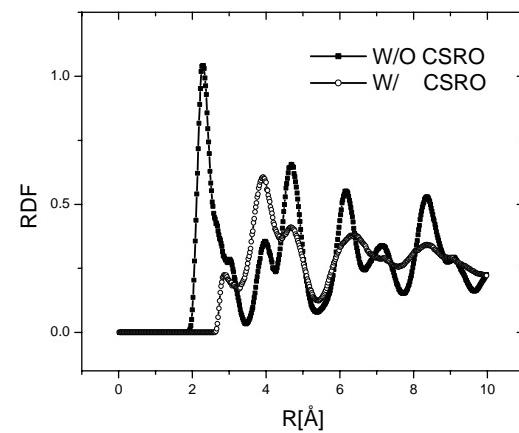


Figure 8. Partial RDF of B atom at above melting temperature (no B-B nearest neighbor with CSRO)

Egami [7] proposed the method of describing the glass transition in metallic glass in terms of the fluctuation in the local stresses. The glass transition is defined as the percolation of the locally collapsed atomic environments, and  $T_g$  is given by,

$$T_g = \frac{2\Omega K}{k_B} (\varepsilon_v^{crit})^2 = 6.14 \times 10^{-3} \frac{\Omega K}{k_B}, \quad (2)$$

where  $\Omega$  is atomic volume,  $K$  is the bulk modulus,  $k_B$  is the Boltzmann constant, and  $\varepsilon_v^{crit}$  is the critical volume expansion for local topological stability. For the present system equation (2) gives  $T_g = 591$  K, using the average values of  $\Omega$  and  $K$ , which is lower than the glass transition temperature observed by the simulation. The fast cooling rate is the reason why the two glass transition temperatures are inconsistent.

This theory was further extended and recently applied to the question of bulk metallic glass formation [2]. A novel concept of local glass transition was introduced, taking note that the topological instability condition that leads to equation (2) can be defined locally. In the binary metallic system, there are four local structure collapses: an “A” atom centered local structure broken by insertion of an “A” atom, an “A” atom centered local structure broken by insertion of a “B” atom, a “B” atom centered local structure broken by insertion of an “A” atom, and a “B” atom centered local structure broken by insertion of an “A” atom. Thus four different local glass transitions can be defined correspond to each scenario. It was found that if the formation of pairs made of two small atoms is prevented, the local glass transition temperature for a small atom is higher than that for a large atom, when  $\Omega K$  is equal. This means that the local environment of a small atom freezes earlier than large atoms during the process of quenching, so the diffusion of the system is suppressed, increasing the viscosity, making crystallization more difficult, and thus improving GFA.

The present simulation confirms this prediction. Without the CSRO the critical size difference for the solute concentration of 0.2 was 13 %. With the CSRO, however, the system with the size factor of 12 % was vitrified, proving the improvement in GFA. Work is in progress to determine the critical size difference with the CSRO.

## CONCLUSIONS

This paper shows that by simply introducing compositional short-range order, the glass forming ability of metallic system is improved. The simulation results can be explained by the recent theory of bulk metallic glass formation through local glass transition and nano-glass formation. The prevention of small and small atomic pairs will result in the increase of the glass transition temperature of the system. The results provide a useful guidance of the selection of new bulk metallic glass.

## ACKNOWLEDGMENTS

This work was supported by the Defense Advanced Research Projects Agency and the Office Naval Research through DARPA/ONR Grant N00014-01-1-0961 and through Boeing Co. Grant 44955-00-00. The author is grateful to S. J. Poon, G. S. Shiflet and W. L. Johnson for useful discussions.

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